Trickle or treat: the dynamics of nutrient export from polar glaciers

Ashley Dubnick[a], Jemma Wadham[b], Martyn Tranter[b], Martin Sharp[a], John Orwin[c] *, Joel Barker[d], Elizabeth Bagshaw[e], Sean Fitzsimons[c].

[a] Department of Earth and Atmospheric Sciences, University of Alberta, Edmonton, AB, T6G 2E3, Canada
[b] Bristol Glaciology Centre, School of Geographical Sciences, University of Bristol, Bristol BS8 1SS, UK
[c] Department of Geography, University of Otago, P.O. Box 56, Dunedin, New Zealand 9054
[d] School of Earth Sciences, The Ohio State University at Marion, 384B Morrill Hall, 1465 Mount Vernon Ave, Marion, OH 43302, USA
[e] School of Earth and Ocean Sciences, Cardiff University, UK, CF10 3AT, United Kingdom

Corresponding author:
Ashley Dubnick
email: adubnick@uaberta.ca
Phone: +1 780 721 5754

Email addresses:
Jemma Wadham: J.L.Wadham@bristol.ac.uk
Martyn Tranter: m.tranter@bristol.ac.uk
Martin Sharp: martin.sharp@ualberta.ca
John Orwin: john.orwin@stantec.com
Joel Barker: barker.246@osu.edu
Elizabeth Bagshaw: BagshawE@cardiff.ac.uk
Sean Fitzsimons: sean.fitzsimons@otago.ac.nz

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Key words: nitrogen, phosphorus, organic carbon, glacier hydrology, Dry Valleys

* Stantec Consulting, 200-325 25 Street SE, Calgary, Alberta T2A 7H8, Canada

1. Abstract

Cold-based polar glacier watersheds contain well-defined supraglacial, ice-marginal, and proglacial elements that differ in their degree of hydrologic connectivity, sources of water (e.g. snow, ice, and/or sediment pore water), meltwater residence times, allochthonous and autochthonous nutrient and sediment loads. We investigated 11 distinct hydrological units along the supraglacial, ice marginal, and proglacial flow paths that drain Joyce Glacier in the McMurdo Dry Valleys of Antarctica. We found that these units play unique and important roles as sources and/or sinks for dissolved inorganic nitrogen (DIN) and phosphorus (DIP), and for specific fractions of dissolved organic matter (DOM) as waters are routed from the glacier into nutrient-poor downstream ecosystems. Changes in nutrient export from the glacial system as a whole were observed as the routing and residence times of meltwater changed throughout the melt season. The concentrations of major ions in the proglacial stream were inversely proportional to discharge, such that there was a relatively constant "trickle" of these solutes into downstream ecosystems. In contrast, NO_3^- concentrations generally increased with discharge, resulting in delivery of episodic pulses of DIN-rich water ("treats") into those same ecosystems during high discharge events. DOM concentrations/fluorescence did not correlate with discharge rate, but high variability in DOM concentrations/fluorescence suggests that DOM may be exported downstream as episodic "treats", but with spatial and/or temporal patterns that remain poorly understood. The strong, nutrient-specific responses to changes in hydrology suggest that polar glacier drainage systems may export meltwater with nutrient compositions that vary within and between melt seasons and watersheds. Since nutrient dynamics identified in this study differ between glacier watersheds with broadly similar hydrology, climate and geology, we emphasize the need to develop conceptual models of nutrient export that thoroughly integrate the

biogeochemical and hydrological processes that control the sources, fate and export of nutrients from each system.

2. Introduction

Glaciers are a primary water source in many polar watersheds and are an important source of macronutrients, including nitrogen (N), phosphorus (P) and carbon (C) (Bagshaw *et al.*, 2013; Bhatia *et al.*, 2013b; Hawkings *et al.*, 2016). Most glacially-derived meltwater originates on the glacier surface (supraglacial environment) and in cold-based glacier systems in the McMurdo Dry Valleys of Antarctica (and many other glacier systems world-wide), this environment contains a number of discrete and relatively well-studied biogeochemical systems including snow, glacier ice, cryoconite holes, cryolakes, and supraglacial streams. The physical differences between these systems result in differences in both allochthonous and autochthonous sources/sinks for nutrients. Atmospheric aerosol deposition and *in situ* biogeochemical processes and microbial activity in supraglacial snowpacks (Hodson, 2006) can lead to the release of meltwaters with high concentrations of dissolved inorganic nitrogen (DIN; Tranter *et al.*, 1993; Hodson *et al.*, 2005) and labile organic matter (Barker *et al.*, 2006, 2009; Dubnick *et al.*, 2010). Microbial activity in cryoconite holes can generate high concentrations of dissolved organic carbon (DOC), nitrogen (DON) and phosphorus (DOP) (Stibal *et al.*, 2008; Bagshaw *et al.*, 2013), even in Blue Ice areas of the East Antarctic ice sheet where DIN may accumulate and is recycled by the cryoconite microbial community (Hodson *et al.*, 2013). These nutrients may be bio-available (Stibal *et al.*, 2008; Anesio *et al.*, 2009; Bhatia *et al.*, 2010; Bagshaw *et al.*, 2013) and can feed downstream ecosystems (Foreman *et al.*, 2004) if the meltwaters connect to streams that transport them across the glacier surface. Surface streams are one of the least favourable biological habitats in the supraglacial system and are characterised by low concentrations of NO_3^- and low nutrient

processing rates, but nitrification and dissolved organic matter (DOM) uptake have nonetheless been observed (Fortner *et al.*, 2005; Scott *et al.*, 2010).

On cold-based glaciers that are frozen to the bed, supraglacial streams transport meltwater across the glacier surface to either an un-channelized ice-marginal zone or a well-defined proglacial stream. This ice-marginal environment has geochemical similarities with the subglacial environments in warm-based and polythermal glaciers since it can host a complex drainage network that includes thin films of water, water-saturated till, and poorly inter-connected ponds. It is also the location where dilute supraglacial meltwater first comes into contact with abundant sediment, some of which may be freshly comminuted, and hence is an area of potentially high geochemical activity (Anderson *et al.*, 2000). Unlike many subglacial regions, the ice-marginal environment is exposed to atmospheric sources of solutes and atmospheric gases (e.g. O_2 and CO_2) that can fuel weathering processes.

Studies of the form, availability, and cycling of glacially-derived nutrients highlight the importance of nutrients in supporting downstream ecosystems (e.g. Hood *et al.*, 2009; Bhatia *et al.*, 2013a; Lawson *et al.*, 2013, 2014; Hawkings *et al.*, 2015). This is particularly evident in the polar desert watersheds of Antarctica's Dry Valleys (Moorhead *et al.*, 1997, 2005; Foreman *et al.*, 2004; McKnight *et al.*, 2004; Barrett *et al.*, 2007; Bate *et al.*, 2008) where glacier runoff is effectively the only source of water and downstream lakes are among the most nutrient-limited aquatic ecosystems on Earth (Parker and Simmons, 1985; Priscu, 1995; Foreman *et al.*, 2004; Dore and Priscu, 2013). The fluxes and timing of nutrient delivery, especially of limiting nutrients, to depauperate downstream ecosystems may play an important role in controlling the rates and timing of primary production in those systems (Bagshaw *et al.*, 2013).

To date, there has been no integrated study of the distinct sources/sinks of macronutrients in Dry Valley watersheds and the nutrient cycling that occurs as waters flow

en route to downstream proglacial ecosystems. Joyce Glacier in the Garwood Valley of Southern Victoria Land, Antarctica, provides a unique opportunity to study these processes. Its watershed includes distinct and accessible supraglacial, ice-marginal and proglacial hydrological units that exhibit variability in flow rates, water levels, and water residence times over the course of a melt season. These hydrological units differ in their degree of hydrologic connectivity, sources of water (e.g. snow, ice, and/or sediment pore water), meltwater residence times, allochthonous and autochthonous nutrient and sediment loads.

This study has two objectives. The first is to evaluate whether/how the distinct hydrological environments encountered by meltwaters passing through Joyce Glacier's supraglacial, ice-marginal and proglacial drainage systems function as sources and/or sinks for dissolved macronutrients (N, P, and C). We predict that each hydrological environment will play a unique role in the meltwater and nutrient dynamics of the whole drainage system because they differ in terms of the degree of contact that occurs between water, geological material, the atmosphere, biotic communities, and allochthonous nutrient sources. We expect nutrient export from the whole system to be sensitive to the fraction of water that passes through each environment, and to the amount of time that water spends in each of them. Our second objective is therefore to evaluate how variations in the routing and transit times of meltwater passing through the combined supraglacial, ice-marginal, and proglacial drainage system affect the export of macronutrients from the system as a whole. Specifically, we seek to determine whether nutrient delivery to downstream ecosystems occurs as a steady "trickle" or as a series of episodic "treats".

3. Methods

3.1. Study Site

The Garwood Valley in Southern Victoria Land, East Antarctica, extends east-west between the East Antarctic Ice Sheet and the Ross Sea (78°1'S, 163°51'E). The area is

considered a polar desert with high winds and very low precipitation, almost all of which falls as snow. The surficial geology of the Garwood Valley consists largely of calcareous aeolian and fluvial sediments and glacial moraines, with exposures of dolomite, granite, and metamorphosed bedrock. Basement rocks are dominated by impure calcareous rocks, with a mineral composition that includes calcite, calc-silicates, phlogopite, pargasite and chondrodite (Williams *et al.*, 1971). Mafic and felsic rocks are also present, and include amphibolites and rocks containing quartz-feldspar-biotite (Williams *et al.*, 1971).

Joyce Glacier, located at the western end of the Garwood Valley, feeds proglacial Holland Stream (Figure 1), which flows along the north-east margin of the glacier and into proglacial Lake Colleen, approximately 750 m from the glacier terminus. This 1 km long lake is permanently ice-covered but develops a moat several meters wide and an outlet channel during the melt season. The outflow of Lake Colleen (Garwood Stream), flows along the terminus of the Garwood Glacier, and enters the Ross Sea ~10 km downstream.

Meltwaters are routed into the Holland Stream via one of two dominant flow paths. Water following the primary flow path originates from supraglacial ice and snow melt, and passes through cryoconite holes, cryolakes, and small supraglacial streams before draining into the ice-marginal environment via gullies along the glacier margin. It then flows through multiple small, poorly-defined streams and/or via shallow subsurface pathways until it reaches the Holland Stream (Figure 1).

Considerably less water follows the second flow path to the proglacial stream. Most of this water originates as ice melt from either the terminal cliffs of Joyce Glacier or the apron of calved ice blocks at their foot. These waters drain through moraines via shallow subsurface pathways and collect in a small proglacial pond that fills and discharges intermittently (typically when melt rates are high) into proglacial Holland Stream via a well-defined channel.

3.2. Data Collection

3.2.1 Discharge monitoring

Holland Stream stage was measured from January 7-31, 2010 at 15 minute resolution using a non-vented HOBO U20-001-04 Water Level Logger (range of 0 to 4 m and accuracy of ± 0.3 cm). The stage data were barometrically compensated using data from a CS100 Setra barometer installed at the Joyce Glacier weather station (see below). Manual flow measurements, made almost daily between January 7th and January 31st, 2010, were used to estimate discharge using the USGS mid-section method, with velocity measured at 0.6 of water depth in each segment of the cross-section (Turnipseed and Sauer, 2010) using a Marsh-McBirney Flo-Mate 2000.

Stage-discharge relationships were established using the *Rating Curve* toolbox in the AQUARIUS™ software suite, using 21 manual discharge measurements. Shift corrections were applied to the stage-discharge rating curve after January 17th to account for the effects of sediment aggradation on the hydraulic geometry. Due to difficulties in generating a stable rating curve, the magnitude of the calculated discharge values should be treated with caution.

3.2.2 Meteorological monitoring

Meteorological conditions on Joyce Glacier were recorded using a Campbell Scientific weather station powered by a solar panel. Measurements were logged every 5 minutes and stored as 15 minute averages in a Campbell Scientific CR1000 data logger and include air temperature and relative humidity (HMP45C sensor), incoming and outgoing short plus long wave radiation (CNR1 net radiometer), and wind speed and direction (RM Young 5103 sensor). .

3.2.3 Sampling

A total of 154 water samples were collected from the supraglacial (cryoconite holes/cryolakes, supraglacial streams), ice-marginal (gullies and pond outflow) and proglacial

(upstream, lake and downstream) environments between January 6 and February 2, 2010. The samples probably do not represent the full range of spatial or temporal variability in water chemistry that exists within each environment. Since the focus of our study is on nutrient dynamics in the proglacial stream, we targeted our sampling of the supraglacial and ice-marginal systems from multiple sites during conditions of high hydrological connectivity/export (between ~11:00 and 18:00) and interpret our results in the context of other studies that more fully capture the temporal and spatial variability of similar environments. We compare daily samples collected in the proglacial (Holland) stream in 2010 with samples from the source areas, as well as samples collected at 2-hour intervals over a 24-hour period on December 9-10, 2008.

Water samples were collected in 1-L plastic Nalgene bottles after rinsing three times with sample. Ice samples were collected using an ethanol-bathed and flame-sterilized steel chisel, and were melted in the field in sterile Whirlpak bags. An aliquot of sample was filtered through sterile 0.7 µm GF/F syringe/filters (rinsed three times with sample prior to use). Two 28-mL universal glass vials were each rinsed three times with filtered sample before being filled and frozen (for dissolved organic carbon (DOC), dissolved organic matter (DOM), and total nitrogen (TN) analyses). This procedure was also followed using 0.45 µm cellulose nitrate filters to fill two 50-mL plastic Nalgene bottles (for major ions) and two 1.5-mL dry glass chromacol vials (for $\delta^{18}O$ and $\delta^{2}H$) for each sample.

3.3. Laboratory Analyses

Concentrations of major ions (Ca^{2+}, K^{+}, Na^{+}, NH_4^{+}, SO_4^{2-}, NO_3^{-}, and Cl^{-}) were determined using a Dionex (DX-500) ion chromatograph (IC) equipped with a GP50 gradient pump and an autosampler with 5 mL polypropylene polyvials (as described by Lawson *et al.*, 2013). For anion analyses, we used an IonPac AS11-HC Hydroxide Selective Anion-Exchange Column (4 x 250 mm) and IonPac AG11-HC Guard Column (2 x 50 mm) with an

ASRS (4mm) suppressor, operated in 100 mA AutoRegen mode with 30 mM sodium hydroxide eluent. For cation analyses, we used an IonPac CS12A Cation-Exchange Column (4 x 250 mm) with CSRS ULTRA II 4 mm suppressor, operated in the 50 mA AutoRegen mode with 20 mM MSA eluent. Detection limits were: Ca^{2+} = 2.0 µeq L^{-1}, K^{+} = 0.26 µeq L^{-1}, Na^{+} = 3.0 µeq L^{-1}, NH_4^{+} = 0.55 µeq L^{-1}, SO_4^{2-} = 2.1 µeq L^{-1}, NO_3^{-} = 0.48 µeq L^{-1}, and Cl^{-} = 2.8 µeq L^{-1} and accuracies were c. 5%. HCO_3^{-} concentrations were taken to be equal to the charge balance error for each sample. Concentrations of PO_4^{3-}, DSi, NO_2^{-} were analyzed using a Bran and Luebbe continuous segmented-flow AutoAnalyser (AA3) based on principles of colorimetry. Detection limits for each ion were: PO_4^{3-} = 0.42 µeq L^{-1}; DSi = 3.2 µM, NO_2^{-} = 0.26 µM, and accuracies were c. 10%.

Total dissolved P was determined using a sulphuric acid/persulphate digestion step (Johnes and Heathwaite, 1992). The samples were autoclaved with an oxidizing solution containing potassium persulphate, boric acid and sodium hydroxide. The samples were then measured colorimetrically on a Shimadzu UVmini-1240 spectrophotometer for total dissolved phosphorus. The detection limit was 1.6 µM and accuracy was <5%. Non-purgeable organic carbon and total nitrogen (TN) concentrations were determined by high temperature combustion (680°C) using a Shimadzu TOC-VCSN/TNM-1 Analyzer equipped with a high sensitivity catalyst. The detection limit for DOC was 17 µM (accuracy of ca. 10%) and 0.7 µM (accuracy of < ca. 5%) for TN. DON was subsequently calculated by subtracting corresponding NO_3^{-} and NH_4^{+} concentrations from TN.

The spectrofluorescent properties of DOM were determined using a Horiba Fluorolog-3 spectrofluorometer equipped with a xenon lamp as an excitation source. Frozen samples were thawed and warmed to room temperature immediately prior to analysis in a sample-rinsed quartz glass cuvette with a 10 mm path length. Synchronous scans were completed by measuring the fluorescence intensity at 1 nm intervals over emission wavelengths between

218 and 618 nm, with an excitation offset of 18 nm, an integration time of 0.5 s, and 10 nm slits. Internal and dark corrections were applied to the results.

3.4. Data Processing and Statistical Analysis

Data were processed in Matlab R2015a. One-way analysis of variance (ANOVA) was used to assess the significance of differences in the concentrations of nutrients between sampling environments (e.g. cryoconite holes vs supraglacial streams). For chemical nutrients with concentrations that were below the analytical detection limit in most samples (i.e. NH_4^+ and PO_4^{3-}), Fisher Exact Tests (FET) were used to evaluate the significance of between-environment differences in the frequency of detection. Where concentrations of a given constituent were above the detection limit in all samples taken from a specific environment, 2-sample t-tests were used to evaluate the statistical significance of concentration differences between environments. Spearman Rank correlations were used to evaluate the significance of dependency between variables within an environment. We acknowledge that because samples were not collected randomly (in space or time), p-values may not accurately reflect the true significance of the differences that exist within or between the hydrological environments sampled in this study. Nonetheless, a p-value of <0.05 was judged to indicate a significant difference for all statistical tests that were applied to the spatially and/or temporally clustered sample data that form the basis to this study.

The spectrofluorescence data were processed and modelled using Principal Components Analysis (PCA) to decompose the complex multivariate signals into linearly independent components (Persson and Wedborg, 2001; Barker *et al.*, 2009), which characterize the variance in the dataset and are interpreted as specific fractions of DOM. Due to the limitations associated with classifying individual components of DOM via fluorescence spectroscopy, particularly when using synchronous scans that cover only a small transect of

the total optical space, we characterize DOM components broadly as being either protein-like (emission peak <350 nm) or humic-like (emission peak >350 nm) (Carstea, 2012).

Relationships between nutrient concentrations and coincident discharge rates (typically measured within 1 hour of sampling) were developed using Locally Weighted Scatterplot Smoothing (LOWESS) with a span of 0.7. Confidence intervals were calculated as ± two times the standard deviation of 1000 LOWESS relationships derived by bootstrapping. The upper and lower confidence intervals from these curves were used to estimate nutrient fluxes at the calculated discharge rates throughout the monitoring period.

4. Results

4.1. Hydrology and major ions

Like other Dry Valley glaciers, Joyce Glacier's energy balance is driven primarily by shortwave radiation, resulting in strong diurnal and seasonal fluctuations in the volume of meltwater produced (Figure 2; Hoffman *et al.*, 2008). Supraglacial snow and glacier ice yielded the most dilute samples, with mean total ion concentrations of 180 μeq L^{-1} and 97 μeq L^{-1}, respectively (Figure 3a). Mean solute concentrations were significantly higher in cryoconite holes (662 μeq L^{-1}), supraglacial streams (596 μeq L^{-1}) and ice-marginal gullies (668 μeq L^{-1}) (ANOVA, $p<0.05$) and continued to increase downstream, including in the ice-marginal pond (1262 μeq L^{-1}) and proglacial environments. Mean solute concentrations increased significantly from the proglacial upstream site (1247 μeq L^{-1}) to the proglacial downstream site (1469 μeq L^{-1}; ANOVA, $p<0.05$), and the concentration of total ions at the proglacial upstream site was negatively correlated with discharge (r_s=-0.64, n=22, $p<0.01$) (Figure 4).

4.2. Dissolved Inorganic Nitrogen

DIN in natural waters consists primarily of NO_3^-, NO_2^-, and NH_4^+, all of which were analyzed in this study. While 83% of meltwater samples contained NO_3^- concentrations

above the detection limit (0.48 µM), only 64% contained NH_4^+ above the detection limit (0.55 µM), and none contained NO_2^- above the detection limit (0.52 µM). Therefore, the discussion of DIN in this study is limited to NO_3^- and NH_4^+, for which both concentration and/or detection rate varied significantly within and between meltwater environments (Figure 3b; Figure 5).

In the supraglacial environment, snow contained the highest average concentration of NO_3^- (5.0 µM,) and glacier ice produced the highest detection rate of NH_4^+ (90% of samples). Supraglacial streams and cryoconite holes, which are fed by snow and ice melt, produced a significantly lower detection rate of NH_4^+ than glacier ice (FET, $p<0.05$) and significantly lower NO_3^- concentrations than snow (ANOVA, $p<0.05$). As supraglacial streams were routed through the ice-marginal gullies, mean NO_3^- concentrations increased from 1.87 µM to 3.25 µM (ANOVA, $p<0.05$). The ice-marginal pond waters contained even higher NO_3^- concentrations than were found in the ice-marginal gully waters (8.61 µM; ANOVA, $p<0.05$), but NH_4^+ was detected in only 50% of samples from these waters. NO_3^- concentrations in the ice-marginal pond were significantly higher than those in potential source waters, including snow, glacier ice, moraine ice, and gully water (ANOVA, $p<0.05$). DIN was depleted and/or diluted in the proglacial stream and lake where the frequency of detection of NH_4^+ and the concentration of NO_3^- decreased from 20% and 1.54 µM at the upstream site to 8% and <0.48 µM at the downstream site, respectively. At the proglacial upstream site, NO_3^- was positively related to discharge ($r_s=0.79$, $n=22$, $p<0.01$; Figure 4).

4.3. Dissolved Inorganic Phosphorus

Only 47% of the meltwater samples in this study contained dissolved inorganic phosphorus concentrations (DIP; PO_4^{3-}) above the detection limit (0.24 µM). However, significant variations in both detection rate and concentration were observed along the flow path (Figure 5). Low concentrations of rock-derived nutrients, including phosphorus, were

found in supraglacial snow and ice (less than 30% of samples contained PO_4^{3-} concentrations above the detection limit). The detection rate of PO_4^{3-} increased significantly from ice to cryoconite holes (FET, $p<0.05$). However, PO_4^{3-} concentrations in cryoconite hole samples were highly variable, with 37% of samples below the detection limit, and others containing the highest concentrations observed among all meltwater samples (i.e. 3.5 µM and 1.6 µM).

All the ice-marginal samples contained PO_4^{3-} concentrations above the detection limit, which is a significantly higher detection rate than for snow (FET, $p=0.02$) and ice (FET, $p=0.002$). Similar to waters from ice-marginal gullies, all samples from the ice-marginal pond contained detectable quantities of PO_4^{3-}, but the average concentration in the pond waters (0.46 µM) was significantly higher than in the gullies (0.34 µM, T Test, $n_1=6$; $n_2=3$, $p<0.01$). All basal ice and moraine ice samples contained detectable quantities of PO_4^{3-}, with concentrations averaging 1.17 µM and 0.49 µM, respectively. Detection of PO_4^{3-} decreased significantly in the proglacial system, from 100% in the ice-marginal gullies to 25% at the upstream proglacial site (FET, $p=0.001$), and 0% at the downstream proglacial site (FET, $p=0.01$).

4.4. Dissolved Organic Matter

Dissolved organic matter (DOM) in the system was assessed by exploring dissolved organic carbon (DOC), nitrogen (DON) and phosphorus (DOP) concentrations and characterizing DOM using spectrofluorescence methods. While all samples contained detectable concentrations of DOC and DON, only 4 samples contained DOP above the detection limit. Although DON comprised most (average of 74%) of the dissolved nitrogen in the meltwater samples, with a mean concentration of 11 µM, no significant differences in DON concentrations were observed between the various meltwater environments (ANOVA, $p>0.05$). Two Principal Components of the fluorescence spectra explained 76.9% and 21.6% of the variance in the dataset, and the remaining components each explained <0.6%.

Component 1 had a prominent emission peak at 330 nm, associated with protein-like moieties, and Component 2 had an emission peak at 405 nm, associated with humic-like moieties (Carstea, 2012).

Although DOC concentrations in supraglacial snow and ice were not measured in this study, previous work reports DOC concentrations of between ~20 µM and 40 µM in supraglacial snow and ice from the Dry Valleys (Bagshaw *et al.*, 2013; Barker *et al.*, 2013). Cryoconite hole waters had an average DOC concentration of 125 µM with a standard deviation of 75 µM (n=13). Despite this variability in DOC concentrations, all cryoconite hole DOM samples had similar spectrofluorescence properties. In addition to strong loadings on Components 1 and 2, cryoconite hole samples contained a prominent peak at 298 nm with a fluorophore-like signal (systematic bell-shaped curve), described by PCA Component 7, suggesting the presence of an additional protein-like moiety (Carstea, 2012). While this component explained only 0.04% of the variability in the total dataset, it had significantly higher loading on cryoconite hole DOM than on DOM from any of the other meltwater environments, including the outflow channels of the cryoconite holes (Figure 3h, ANOVA, $p<0.05$). Component 7 was negatively correlated with deuterium excess (r_s=-0.56, n=15, p=0.03) and air temperature (r_s=-0.63, n=10, p=0.05), suggesting that melt-refreeze cycling, evaporation effects and/or weather conditions may affect its abundance.

DOC concentrations decreased by more than 50% between supraglacial streams ($\bar{x}$ = 131 µM) and ice-marginal gullies ($\bar{x}$ = 54 µM), but increased again by a factor of approximately 3.5 in the ice-marginal pond ($\bar{x}$ = 192 µM, the highest mean DOC concentration among all meltwater environments). The ice-marginal pond water also yielded the highest fluorescence of the humic-like Component 2 DOM fraction, and the highest C/N ratio.

The proglacial stream contained some of the lowest DOC concentrations measured, and displayed significantly less protein-like Component 1 fluorescence than was found in the supraglacial stream (ANOVA, $p<0.05$), and significantly less humic-like Component 2 fluorescence than the ice-marginal pond (ANOVA, $p<0.05$). In the proglacial stream, DOC concentrations and DOM characteristics remained relatively constant between the upstream and downstream monitoring sites, displaying no significant differences (ANOVA, $p>0.05$), despite the relative abundance of algal mat communities in the littoral zone of the proglacial lake and in stable, slow-flowing sections of the stream. Neither DOC concentrations nor the fluorescence intensity of the DOM components varied significantly with proglacial stream discharge (r_s=0.12, n=22, p=0.58), but DOC concentrations were significantly higher in January 2010 ($x\square$ = 88 μM) than in December 2008 ($x\square$= 21 μM; T test, n_1 = 6; n_2 = 22, $p<0.05$) and they varied considerably throughout both melt seasons (σ = 47 μM).

5. Discussion

5.1. Nutrient sources and sinks along the flow path

5.1.1 Supraglacial Environments

Most water in the Garwood Valley originated from supraglacial snow or ice melt, in which NO_3^- and NH_4^+ concentrations were high (Figure 3; Figure 5; Figure 6). DIN in snow and ice can be derived from atmospheric sources via snowfall or dry deposition. Cryoconite holes and cryolakes functioned as a sink for NH_4^+ and NO_3^- and as a source of PO_4^{3-} and the protein-like DOM Component 7 in this study (Figure 3, Figure 5; Figure 6). They are widely known as active biogeochemical systems (Bagshaw *et al.*, 2007; Hodson *et al.*, 2010; Tranter *et al.*, 2010) and their nutrient dynamics are important because waters that pass through them comprise a significant portion of supraglacial runoff meltwater (Fountain *et al.*, 2004).

Cryoconite holes and cryolakes facilitate relatively prolonged and extensive rock-water contact, which can add rock-derived nutrients, such as DIP, to the solute-poor meltwaters.

Geochemically active biota have been observed in cryoconite holes, which are known to assimilate inorganic nutrients (including DIN and DIP) in the production of organic material (Hodson *et al.*, 2005) and play an important role in defining the biogeochemistry of supraglacial waters and the range of nutrients exported to downstream ecosystems (Bagshaw *et al.*, 2010, 2013, 2016a). For example, the DIN requirements of primary producers in cryoconite holes in Antarctic blue-ice environments exceeds rates of DIN supply from ice melt at the base of the hole, suggesting that DIN is actively recycled within these systems and that they are likely to have an important influence on the nitrogen economy of supraglacial waters (Hodson *et al.*, 2013). DIN may also be utilized by microbes as an electron acceptor in energy-producing redox reactions such as denitrification (Hodson *et al.*, 2010; Telling *et al.*, 2011). Although nitrogen cycling in cryoconite holes and supraglacial streams can be complex, studies have identified the occurrence of nitrification (Baron *et al.*, 1995; Hodson *et al.*, 2005; Scott *et al.*, 2010), denitrification (Hodson *et al.*, 2010; Telling *et al.*, 2011), nitrogen assimilation (Hodson *et al.*, 2005) and the production of particulate nitrogen (Bagshaw *et al.*, 2013).

Biological activity in cryoconite holes likely results in long-term net carbon fixation, which may be an important source of DOM for nutrient-poor downstream ecosystems (Bagshaw *et al.*, 2016a) and, potentially, the protein-like DOM (Component 7) observed in this study. The relative abundance of this DOM fraction in cryoconite holes and cryolakes, and its depletion downstream, suggest that this fraction of the DOM pool may be labile and provide a metabolic substrate for downstream ecosystems. Other studies have identified similar autochthonous/microbial/protein-like DOM compounds in cryoconite holes world-wide (Lawson *et al.*, 2013, 2014; Pautler *et al.*, 2013) and uniquely supraglacial fractions of DOM which are likely labile (Bhatia *et al.*, 2010; Dubnick *et al.*, 2010; Barker *et al.*, 2013; Lawson *et al.*, 2014), show non-conservative behaviour, and are depleted in downstream

ecosystems (Barker *et al.*, 2006, 2013; Hood *et al.*, 2009; Scott *et al.*, 2010) by biotic or abiotic processes (e.g. photochemical reactions).

5.1.2 Ice-marginal Environments

Solute-poor meltwaters from the supraglacial environment are routed into sediment-rich ice-marginal gullies, where large increases in NO_3^- occur (Figure 3b; Figure 6). A large portion of DIN supplied to meltwaters in the ice-marginal system may be sourced from the dissolution of nitrogen-containing salts. Low precipitation rates, humidity, and overland flow allow salts to accumulate in Dry Valley soils, similar to other arid regions where evaporation and sublimation exceed precipitation (Bisson *et al.*, 2015). Nitrates of sodium and magnesium, including Darapskite ($Na_3NO_3SO_4H_2O$) and soda niter ($NaNO_3$), are widespread in South Victoria Land (Claridge and Campbell, 1968; Keys and Williams, 1981), are highly soluble and, if present, could readily contribute NO_3^- to meltwaters. The ice-marginal water chemistries observed here are similar to those observed in ice-marginal ponds elsewhere in the Dry Valleys where the dissolution of atmospheric aerosols (e.g. HNO_3, $(NH_4)_2SO_4$) and nitrate-bearing salts contribute significantly to the solute load (Healy *et al.*, 2006; Wait *et al.*, 2006; Webster-Brown *et al.*, 2010).

Biogeochemical activity in the ice-marginal system may also supply meltwaters with DIN. Active microbial communities, which are likely important in N cycling, have been identified in recently deglaciated ice-marginal soils (Strauss et al., 2012). Studies of freshly-exposed, ice-marginal soils report that in situ N-cycling is initially dominated by nitrogen mineralization via the decomposition of organic matter (<10 yrs exposed), followed by N-fixation (50 to 70 years exposed) (Brankatschk et al., 2011). Other studies have identified the presence of nitrification in ice-marginal environments (Wynn *et al.*, 2007; Hodson *et al.*, 2009; Ansari *et al.*, 2012), and suggest that the amount of NO_3^- derived from nitrification can exceed that derived from atmospheric deposition (Roberts *et al.*, 2010).

There may be similar sources of DIN along the secondary flow path where meltwaters are routed from the apron of calved ice blocks along the terminus and the vertical ice cliffs to the ice-marginal pond. The ice-marginal pond was the most nutrient-rich environment along the flow path and contained the highest concentrations of DIN and DIP. These high concentrations may result from extensive access to nitrogen-containing salt deposits and longer contact with relatively phosphorus-rich glacial till (Gudding, 2003) as waters follow spatially and temporally dynamic flow paths in the shallow subsurface between the glacier terminus and the pond. Pond waters may also acquire DIN and DIP from the melting of basal ice, which is found in nearby ice-cored moraines. Basal ice usually contained NH_4^+ at concentrations at least an order of magnitude higher than found in most other environments, which could be oxidized to NO_3^- by nitrifying bacteria in the hyporheic zone or the soil, as has been reported for other Dry Valley streams (McKnight *et al.*, 2004) subglacial and ice-marginal sediments (Wynn *et al.*, 2007; Hodson *et al.*, 2009; Ansari *et al.*, 2012).

Pond water maintained high DIN and DIP concentrations despite the presence of abundant algae that likely function as a sink for inorganic nutrients. Extensive phytoplankton and microbial mat communities dominated by cyanobacteria have been observed in other Dry Valley ice-marginal ponds (Webster-Brown *et al.*, 2010). The presence of algal communities in the pond may also affect the DOM characteristics of these waters. The ice-marginal pond waters had the highest fluorescence of the humic-like Component 2 DOM fraction and the highest C/N ratio of all meltwater environments sampled (Figure 3d,f). Both observations are consistent with the presence of humic substances that fluoresce at long wavelengths and have relatively high C content, and they suggest that the ice-marginal pond may be a source of humic DOM. Although humic DOM is typically produced by terrestrial vascular plants, which are absent from the Garwood Valley, a similar humic-like fluorescent component can be produced in aquatic environments by the microbial degradation of phytoplankton DOM

(Stedmon and Markager, 2005). Previous studies suggest that production and consumption of similar humic-like DOM can occur very rapidly, and that degradation can occur by microbial and photochemical processes (Stedmon and Markager, 2005).

Although the ice-marginal zone is a potentially important source of nutrients to downstream ecosystems, nutrient transfer from the ice-marginal pond to the proglacial stream occurs only intermittently. Outflow from the ice-marginal pond was typically active only during the daily flow peak (~12:00-24:00), on days with high solar radiation and/or during seasonal peak melt conditions (~Jan/Feb). The hydrology of the ice-marginal zone therefore plays an important role in the timing of nutrient transport to the proglacial stream.

5.1.3 Proglacial Environments

DIN and DIP are supplied to meltwaters in the supraglacial and ice-marginal environments and are likely depleted in the proglacial stream. Decreases in DIN and DIP concentrations have been observed in other Dry Valley proglacial streams and have usually been attributed to nutrient uptake by benthic algal communities and mosses (McKnight *et al.*, 1998, 1999, 2004). Microbial processes in the hyporheic zone, including denitrification and dissimilatory NO_3^- reduction to NO_2^- and NH_4^+, are also likely to contribute to DIN losses (Maurice *et al.*, 2002; McKnight *et al.*, 2004), however these losses are likely minor in comparison to those attributable to benthic algal communities (McKnight *et al.*, 2004). Dry Valley streams and lake ecosystems have been identified as among the most nutrient-poor ecosystems on Earth (Vincent and Vincent, 1982; Parker and Simmons, 1985; Priscu *et al.*, 1989; Priscu, 1995; Dore and Priscu, 2013) and consequently have a high capacity for nutrient uptake (McKnight *et al.*, 2004).

5.2. Trickle or Treat: hydrologically controlled nutrient dynamics

Distinct biogeochemical environments exist in the supraglacial, ice-marginal and proglacial systems explored in this study (Figure 6). Nutrient fluxes from the entire system

are therefore likely to be sensitive to the proportions of water that are routed through each individual environment, and their respective residence times. The strong variability in meltwater fluxes and flow routing at daily, seasonal, and inter-annual timescales that is observed in the Dry Valleys led us to hypothesize that there would be a corresponding dynamic in the mix and quantity of nutrients exported to downstream ecosystems under changing hydrological regimes. To explore this hypothesis, we examined the relationship between discharge and nutrient concentrations and fluxes in the Holland Stream (upstream site) to determine whether nutrient export from the glacial system throughout the melt season occurs as a constant "trickle" or as a series of episodic "treats".

We found differences in the dynamics of nutrient export to downstream environments under changing discharge regimes. The concentrations of most solutes in proglacial stream water are controlled primarily by chemical weathering of the highly permeable, unconsolidated sediments found in the channel margins and hyporheic zone (Gooseff *et al.*, 2004) including carbonate and silicate weathering, and by salt dissolution (Lyons *et al.*, 1998; Maurice *et al.*, 2002; Fortner *et al.*, 2005). Weathering takes place where source material is supplied directly to the channel by aeolian transport, atmospheric deposition (Fortner *et al.*, 2005, 2013) and/or bed/bank erosion. It is unsurprising then, that the concentrations of these solutes increased in the ice-marginal gullies and proglacial stream where rock-water contact was high (Figure 3), and that they increased along both flow paths that fed the proglacial stream. Because the acquisition of these solutes requires prolonged rock-water contact, it is also unsurprising that their concentrations in the proglacial stream decreased with inverse proxies for residence time along both flow paths, including air temperature, incident solar radiation, and discharge (Figure 4). Consequently, downstream ecosystems receive relatively high concentrations of rock-derived solutes during low flow conditions and relatively low concentrations during high flow conditions, producing a relatively steady downstream

"trickle" of such solutes (Figure 7), as has been observed in other Dry Valley streams (Lyons *et al.*, 2003; Fortner *et al.*, 2013).

NO_3^- displayed a different hydrologic dynamic, where its concentration in upstream sections of the proglacial stream generally increased with discharge and the highest concentrations were observed at relatively high discharges (Figure 4). Flux estimates derived from this concentration-discharge relationship suggest that, during high flow conditions, NO_3^- is exported in stronger pulses of DIN rich "treats" than is the case for most solutes (Figure 7). While not every high discharge event corresponds with a DIN "treat", particularly late in the melt season (e.g. January 29), a relatively large portion of the seasonal flux of NO_3^- occurs in pulses at times of high discharge.

The DIN sources and sinks identified along both flow paths (Figure 6) indicate a number of potential mechanisms that may together facilitate the delivery of episodic pulses of DIN during high discharge events. First, high melt/flow rates may allow more extensive wetting of the ice-marginal zone, where waters can access new stores of reactive geologic nitrogen and accumulated NO_3^- bearing salts. This may be particularly true early in the melt season when sediments are first wetted. Second, the ice-marginal zone along the secondary flow path, where DIN acquisition occurs (Figure 6), has relatively large meltwater storage capacity (in ice-marginal ponds and sediments) and only exports meltwater (and therefore DIN) under high melt/flow. Third, the DIN sinks along the flow paths likely consist of ecosystems that consume DIN via processes such as microbial denitrification and nitrogen assimilation. Under high flow conditions, waters containing DIN may travel downstream too rapidly for DIN to be assimilated or converted to N_2 by biota in the upper reaches of the watershed. Therefore, major sources of NO_3^- are likely maximized and major sinks of NO_3^- are likely minimized under conditions of high melt and runoff, allowing DIN to be mobilized and transported downstream as DIN-rich "treats" during pulses of high discharge.

The hydrological dynamics of DOM in the proglacial stream are considerably more complex than those of total ions and NO_3^-, as there is a less consistent relationship between DOC concentrations/DOM composition and either discharge or other indicators of hydrological routing or runoff rate (e.g. solar radiation, air temperature, or total ion concentrations). DOM cycling in glacier systems is likely complex due to the presence of multiple sources (e.g. kerogen/fossil soil carbon, airborne organic matter, necromass, excretions from plants and other organisms), modes of transformation, and sinks (e.g. consumption, decomposition) that remain poorly understood. The lack of dominant source and sink locations for DOM along the flow path (Figure 6) and the complexity of DOM cycling processes likely contribute to the high variability in DOC concentrations and DOM characteristics observed in this study. While neither DOC concentrations nor DOM characteristics appear to be directly influenced by discharge rates, DOC concentrations were significantly higher in January 2010 ($\bar{x}$ = 88 µM) than in December 2008 ($\bar{x}$ = 21 µM), and showed considerable variability throughout both melt seasons (σ = 47 µM). Therefore, while DOC may be delivered to downstream ecosystems in episodic pulses ("treats"), these DOC-rich pulses may not occur at times of high discharge as consistently as the NO_3^- "treats". Because DOC concentrations and DOM characteristics in Dry Valley proglacial streams show high variability both within and between catchments (e.g. McKnight *et al.*, 2001; Barker *et al.*, 2006, 2013) hydrologic controls on DOM fluxes in proglacial streams may also be inconsistent.

While we have established general relationships between total solutes and nitrate and proglacial stream discharge, considerable scatter exists (Figure 4), likely because watershed hydrology and biogeochemical environments evolve over the melt season. This evolution may involve, for example, changes in the rates of primary production in cryoconite holes due to seasonal variations in light intensity and air temperature (Bagshaw *et al.*, 2016b), changes

in the chemistry of ice-marginal pond outflow due to vertical mixing in response to the effects of wind, precipitation, evaporation, and/or temperature (Wait *et al.*, 2006), changes in the availability of nitrate from the dissolution of salts if supplies become depleted as the melt season progresses, and changes in biological nutrient sources/sinks as microbial, benthic algae, and moss communities develop during the growing season (McKnight *et al.*, 1998, 1999, 2004). Similarly, evolution of the hydrological system may involve flushing of the supraglacial environment during periods of rapid melt, expansion of the hyporheic zone and active layer over the summer, and erosion and sedimentation which can reconfigure supraglacial, ice-marginal, and proglacial drainage systems. The co-evolution of biogeochemical and hydrological systems suggests that the dynamics of nutrient export from these systems may change over time.

Although the negative relationship between solute concentration and discharge (Figure 4) is a relatively consistent observation in glacier systems, the strength of this relationship show spatiotemporal variability between Dry Valley (Lyons *et al.*, 2003; Fortner *et al.*, 2013) and other polar glacier watersheds (Wadham *et al.*, 1998; Brown, 2002; Yde *et al.*, 2014). Even more variability is found among polar glacier systems in the case of DIN concentration vs discharge relationships. While we observed a positive relationship between NO_3^- concentration and discharge in the Holland Stream, these parameters were found to be unrelated at a polythermal glacier in the Swiss Alps (Tockner *et al.*, 2002), and inverse relationships have been observed in nearby Taylor Valley proglacial streams (Howard-Williams *et al.*, 1989; Fortner *et al.*, 2013), a polythermal glacier in Greenland (Wadham *et al.*, 2016) and a temperate alpine glacier in the Canadian Rockies (Lafrenière and Sharp, 2005). However, the strengths of these inverse relationships and the degree of scatter show considerable spatiotemporal variability. Proglacial NO_3^- concentration vs discharge relationships in waters draining a polythermal glacier system in Greenland (Leverett Glacier,

Wadham *et al.*, 2016) and a cold-based Glacier in the Dry Valleys of Antarctica (Canada Glacier; Fortner *et al.*, 2013) are more similar to each other than those draining two nearby, cold-based glacier systems that have fundamentally similar glacier hydrology, biogeochemical systems along the flow path, climate and geology (i.e. Joyce Glacier and Canada Glacier). Thus, while there is merit in making broad assumptions about the nutrient dynamics based on macro-scale glaciology and hydrology (e.g. cold-based vs warm-based glacier systems) and upscaling from measurements on one watershed to produce regional nutrient flux estimates (e.g. Bhatia *et al.*, 2013a; Hawkings *et al.*, 2016; Wadham *et al.*, 2016) and estimating nutrient fluxes under future climate conditions (e.g. Hawkings *et al.*, 2015), this study suggests that the detail of watershed biogeochemistry and hydrology in defining proglacial nutrient dynamics and spatiotemporal variability in fluxes may be substantial. The influence of nutrient-specific, watershed-specific, and temporal variability on the dynamics of nutrient fluxes from polar glacier systems is not a new theme for studies of the chemistry of glacially-derived meltwater. However, this study also underlines the important influence of dynamic changes in the connectivity of glacier-proglacial biogeochemical systems on nutrient fluxes (Gooseff *et al.*, 2016) and emphasizes the need to develop conceptual models that thoroughly describe the biogeochemical and hydrological components of the systems.

6. Conclusions

This study identifies a series of distinct biogeochemical environments in the supraglacial, ice-marginal and proglacial systems of Joyce Glacier in Southern Victoria Land, East Antarctica. While dissolved organic nutrient concentrations (DOC, DON and DOP) were either below our detection limits or showed little variability between these environments, potential sources and sinks for DIN, DIP and specific fractions of organic matter were identified. Specifically, snow, glacier ice, and the ice-marginal zone were important sources of DIN, and cryoconite holes and supraglacial and proglacial streams were

sinks for DIN. Cryoconite holes, cryolakes, supraglacial streams and the ice-marginal environment were sources of DIP, which were likely utilized in the proglacial system.

Seasonal changes in the routing and residence times of meltwaters through the various biogeochemical environments along the flow path yielded nutrient-specific dynamics. The concentration of solutes (total ions) decreased with increasing meltwater discharge and resulted in a relatively constant "trickle" of solutes to downstream ecosystems. In contrast, DIN concentrations increased with discharge, resulting in episodic pulses of DIN-rich "treats" during high discharge events. While DOC concentrations did not correlate with discharge rate, high variability in DOC concentrations may indicate that DOC is also exported downstream as episodic "treats", but that the timing of these "treats" may not coincide with peak discharge conditions as consistently as is the case for DIN. These nutrient-specific dynamics are not always consistent between proglacial streams in watersheds with similar climates, geology, and/or glacial thermal regimes, highlighting the important influence of dynamic changes in the connectivity of glacier-proglacial biogeochemical systems on nutrient fluxes (Gooseff *et al.*, 2016) and emphasizes the need to develop conceptual models that thoroughly describe the biogeochemical and hydrological components of the systems.

7. Acknowledgements

This research was supported by Antarctica New Zealand logistics funding for event K064 to S. Fitzsimons and J. Orwin, an NSERC Discovery grant to M. Sharp (155194-2010), an EPSRC grant to J.L. Wadham (EP/D057620/1), the Leverhulme Trust (Phillip Leverhulme Prize to J.L. Wadham, Leverhulme Fellowship to J.L. Wadham), a W. Garfield Weston Award for Northern Research and NSERC CGSD Award to A. Dubnick. We are grateful for Dr C. Butler who contributed to the analytical work.

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Table 1

Environment	Description	# of sites	# of samples (2010 only)
Cryoconite holes /Cryolakes	Representing both open and ice lidded systems near the margin of the Joyce Glacier	7	20
Supraglacial Streams	Representing cryoconite holes/cryolake outflow streams and larger cumulative supraglacial streams	10	22
Gullies	At the glacier margin between the supraglacial and moraine environments	3	7
Pond	At the inflow to the Holland stream	1	5
Upstream	Daily samples immediately downstream of the tributary inflow	1	28
Lake	At the moat on the north shore of the Proglacial Lake	1	5
Downstream	Daily samples from the outflow of the proglacial lake (upstream of Garwood Glacier inflows)	1	26
Snow	Supraglacial and fresh proglacial snow	10	10
Glacier Ice	From ice cliff exposures and the supraglacial environment	16	16
Moraines	Ice cored moraines from within 100 m of the glacier terminus	5	5
Basal Ice	Joyce Glacier basal ice	5	5

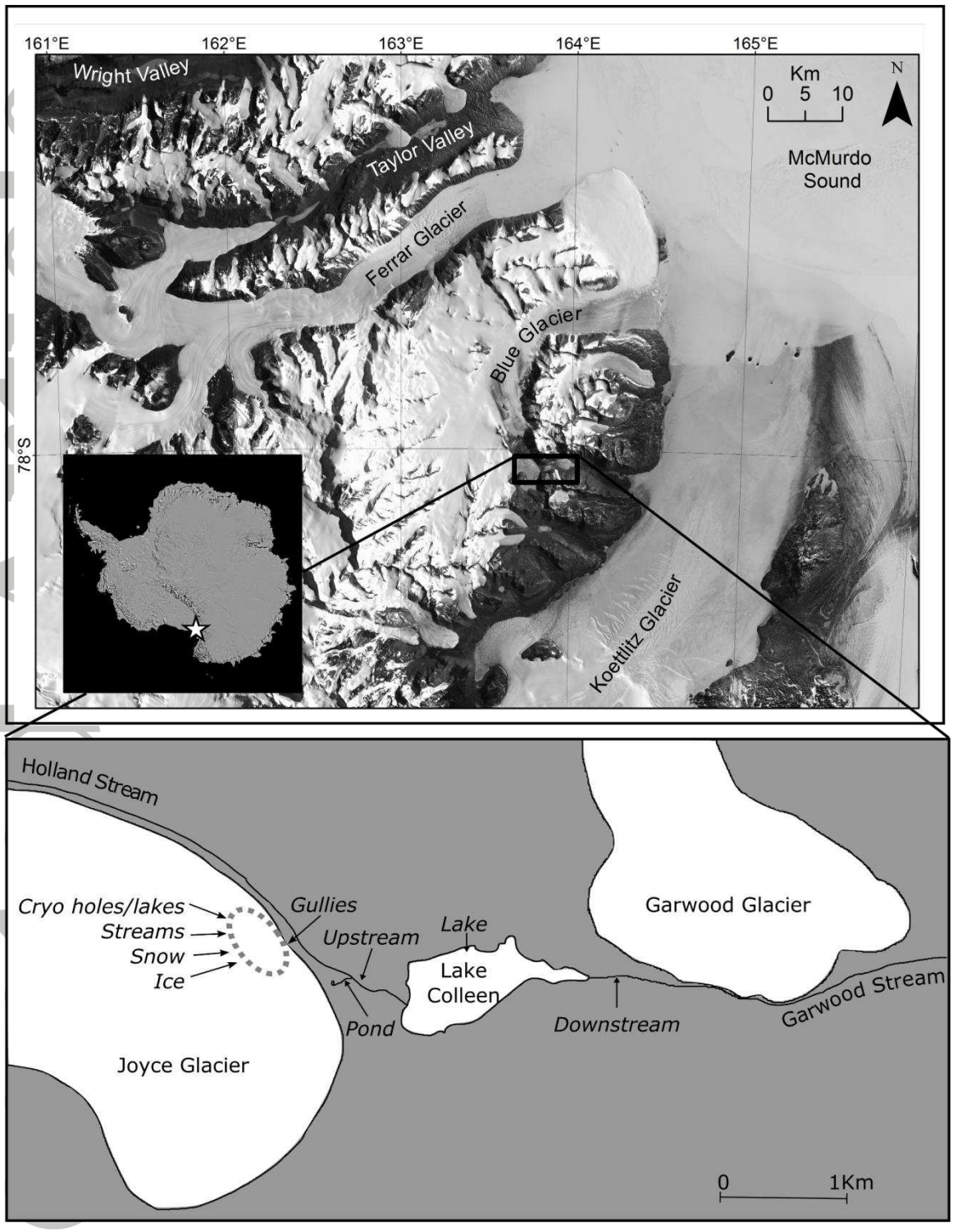

Figure 1: Location of the Garwood Valley (top) and study site (bottom) indicating sample locations in italics. Supraglacial samples (cryoconite holes/cryolakes, streams, snow and ice) were collected within the region indicated by the grey dotted line on the Joyce Glacier.

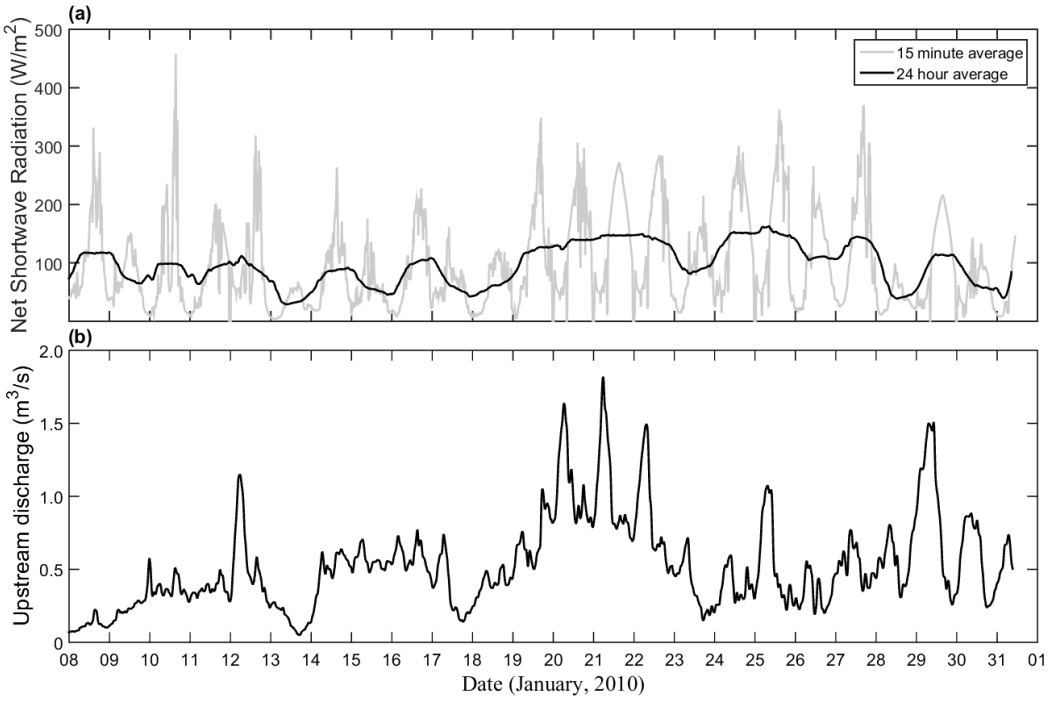

Figure 2: (a) Net shortwave radiation on the Joyce Glacier at 15 minute and 24 hour running averages. (b) Discharge rates at the "upstream" (Holland Stream) monitoring site during the study period.

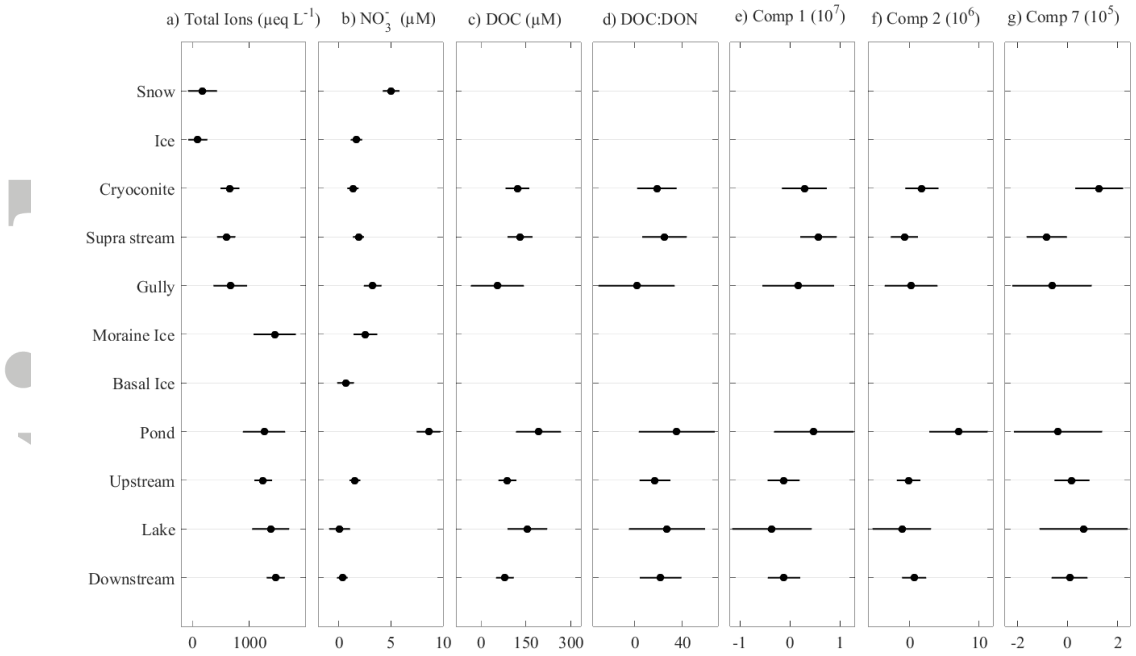

Figure 3: ANOVA with Tukey's range test for various biogeochemical parameters along the flow path. Circles represent the mean and lines indicated the 95% confidence intervals.

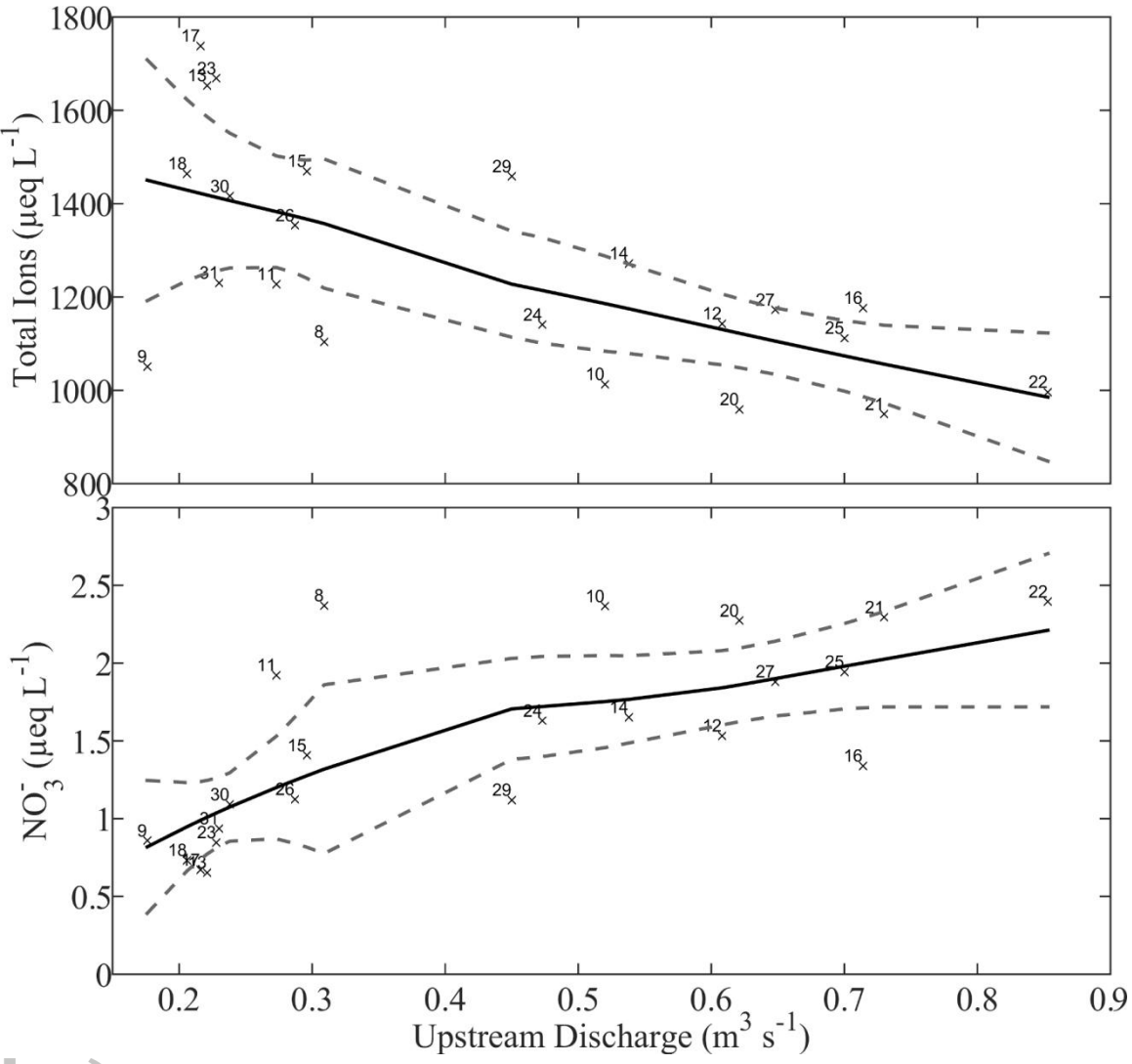

Figure 4: Concentration and fluxes of total ions (top) and nitrate (bottom) in the Holland Stream (Upstream Site). x represent the concentrations measured in samples vs the discharge in the stream at the time of sampling and the number corresponds to the day of month for each data point. The black solid line represents the concentration-discharge relationship determined via LOWESS smoothing, and the dashed grey line indicates the confidence intervals (calculated as ± two times the standard deviation of 1000 LOWESS curves derived by bootstrapping).

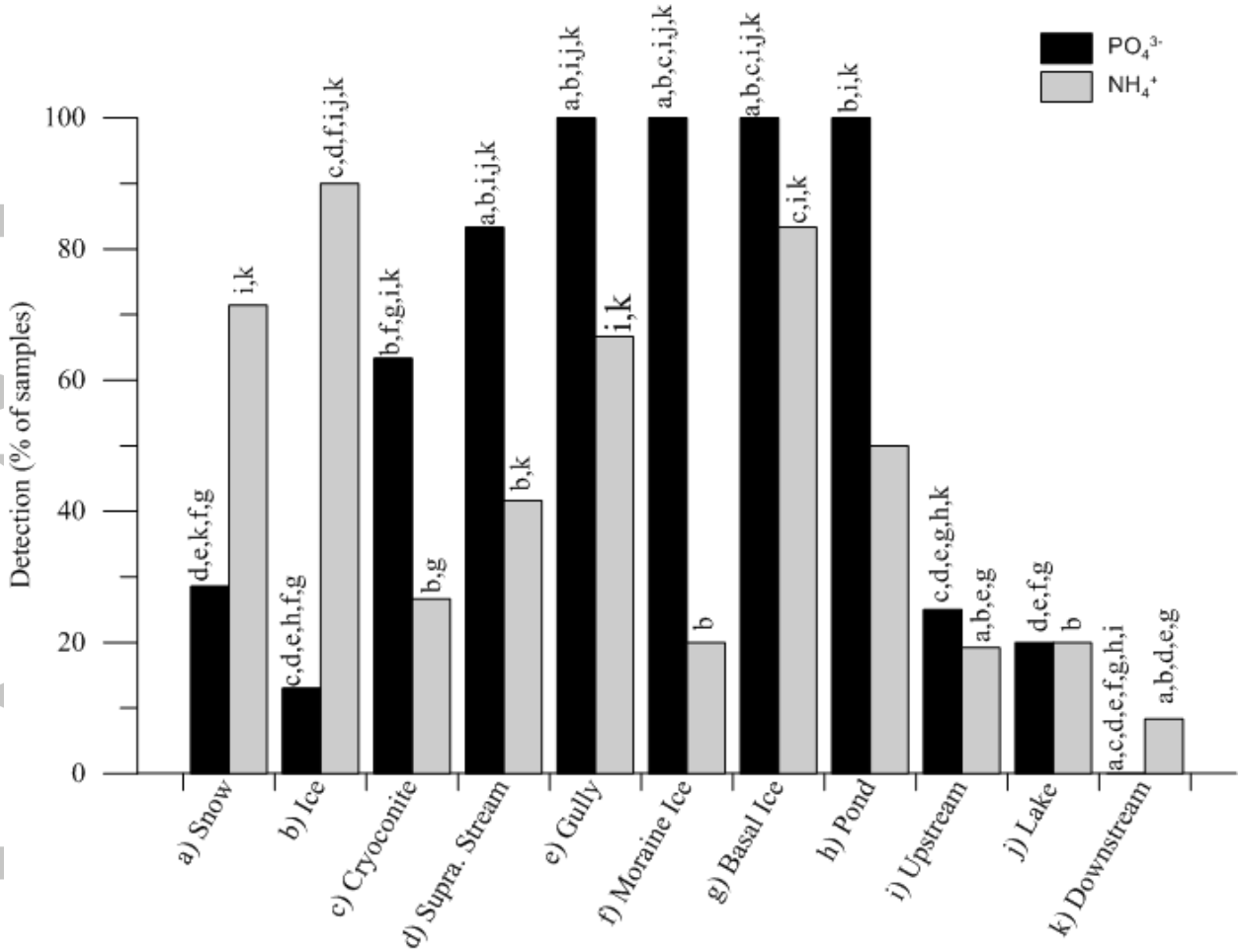

Figure 5: Percentage of samples above the PO_4^{3-} and NH_4^+ detection limits. Letters above each bar indicate significant differences with other environments. Significance was determined using Fisher's exact test (FET) and $p<0.05$.

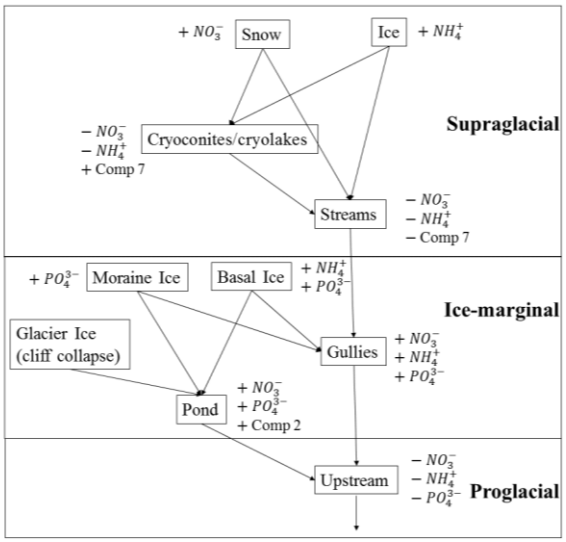

Figure 6: Summary of the sources and sinks for organic and inorganic nutrients in the supraglacial, ice-marginal and proglacial environments. Arrows indicate flow paths, "+" indicate sources, "-" indicate sinks.

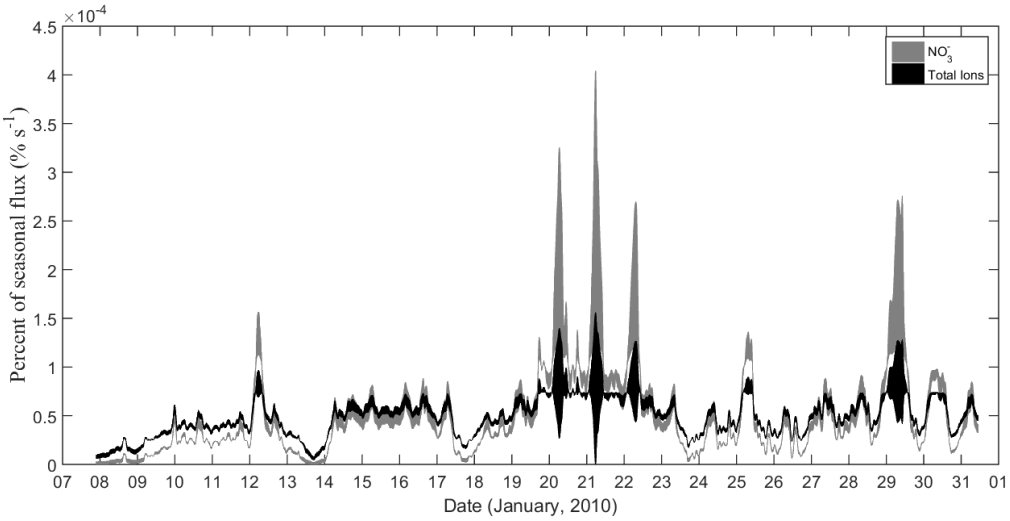

Figure 7: Estimated total ion and NO_3^- fluxes in the Holland Stream (Upstream site) over the study period. Ranges were calculated using the upper and lower confidence intervals presented in Figure 4.